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13. ABSTRACT *(Maximum 200 words)*

This report summarizes the successes of our effort for the HEDM program, both methodological and in terms of metastable molecule chemistry. Recognizing the prospects for highly energetic metastable species based upon nitrogen, we initiated our study of a variety of such potential molecules. These included N_3H_3 , which is isoelectronic with the well-known species ozone, cyclopropane and propene; tetrahedral N_4 which is isovalent with P_4 or As_4, and is forbidden by symmetry from decaying to ground state N_2 molecules; octahedral N_8, isoelectronic with cubane and similarly forbidden from direct decomposition to N_2 in its ground state; and pentazole, HN_5. Each of these was found to contribute a metastable minimum on the global potential energy surface, which also provided the IR spectra of these unknown molecules. At the CC/MBPT level of approximation the vibrational frequencies are normally within 5% of experiment and the relative intensities typically to within about 20. Other work includes studies of transients involved in pertinent oxidation processes like H_2CO_2 and OCBO, and our new approach to excited states, EOM-CCSD.

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March 19, 1996

Dr. Michael R. Berman
Program Manager, Directorate of Chemistry and Life Sciences
Air Force Office of Scientific Research/NL
110 Duncan Avenue, Suite B115
Bolling AFB, DC 20332–0001

Dear Michael,

Enclosed is the final report for HEDM, Grant No. AFOSR-F49620–92–J-0141, which with its no cost extension extended through 1995. I am pleased with our success, both in terms of applications and significant new method development. Considering the demands that have to be met, it may be unique that *five* of our papers under this grant were published as rapid communications by JACS! Of course, my explantation is that when targeting "real" chemists for one of my papers, more than two pages of text exceeds my (and their?) concentration level.

See you in Boulder if not before.

Best regards,

Rodney J. Bartlett
Graduate Research Professor
of Chemistry and Physics

R.J. Bartlett • H.-P. Cheng • E. Deumens • J.L. Krause • P.-O. Löwdin • D.A. Micha
H.J. Monkhorst • N.Y. Öhrn • J.R. Sabin • S.B. Trickey • M.C. Zerner

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FINAL REPORT

AIR FORCE
HIGH ENERGY DENSITY
MATERIALS (HEDM) PROJECT

Grant No. AFOSR-F49620-92-J-0141
01/01/92 through 01/31/96

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Quantum Theory Project
University of Florida
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This report summarizes the successes of our effort for the HEDM program, both methodological and in terms of metastable molecule chemistry. Recognizing the prospects for highly energetic metastable species based upon nitrogen, we initiated our study of a variety of such potential molecules. These included N_3H_3 , which is isoelectronic with the well-known species ozone, cyclopropane and propene; tetrahedral N_4 which is isovalent with P_4 or As_4, and is forbidden by symmetry from decaying to ground state N_2 molecules; octahedral N_8, isoelectronic with cubane and similarly forbidden from direct decomposition to N_2 in its ground state; and pentazole, HN_5. Each of these was found to contribute a metastable minimum on the global potential energy surface, which also provided the IR spectra of these unknown molecules. At the CC/MBPT level of approximation the vibrational frequencies are normally within 5% of experiment and the relative intensities typically to within about 20. Other work includes studies of transients involved in pertinent oxidation processes like H_2CO_2 and OCBO, and our new approach to excited states, EOM-CCSD.

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Summary of Principal Recent Results

To date, the successes of our effort for the HEDM program, both methodological and in terms of metastable molecule chemistry have been many. Considering the latter first, recognizing the prospects for highly energetic metastable species based upon nitrogen, we initiated our study of a variety of such potential molecules. These included N_3H_3 [1]*, which is isoelectronic with the well-known species ozone, cyclopropane and propene; tetrahedral N_4 [6] which is isovalent with P_4 or As_4, and is forbidden by symmetry from decaying to ground state N_2 molecules; octahedral N_8 [6], isoelectronic with cubane and similarly forbidden from direct decomposition to N_2 in its ground state; and pentazole, HN_5 [5]. Each of these was found to contribute a metastable minimum on the global potential energy surface. The minima were fully characterized by calculation of the Hessian (second derivative matrix) frequently using our recently developed analytical gradient CC/MBPT methods, which also provided the IR spectra of these unknown molecules. At this level of approximation the vibrational frequencies are normally within 5% of experiment and the relative intensities typically to within about 20% [6]. I might add, the character of a critical point on an energy surface can change depending upon whether electron correlation is included, so this is a critical test for every potential metastable molecule. Furthermore, some regard must be paid to low-lying excited states that might offer a decomposition path to ensure that the molecule is stable to unimolecular decomposition. In the absence of matrix isolation, bimolecular mechanisms can also offer ways to prohibit the existence of any such proposed molecule.

Although sometimes postulated, there is no experimental evidence for the existence of any of these molecules. This tends to be a recurring theme in the investigation of metastable molecules. Yet, the accuracy of modern *ab initio* correlated predictions is sufficiently reliable that barring rapid bimolecular kinetics and certain possible excited state decomposition paths, the proposed metastable molecule should be capable of synthesis at least in matrix isolation and can be identified from our predicted frequencies.

*References are to HEDM publication list, pgs. 15, 16.

A. Metastable Molecules

1. The nitrogen aromatic analogue of benzene, hydrogen pentazole,

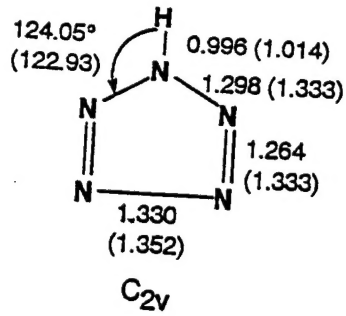

Figure 1 Hydrogen Pentazole Molecule

has never been observed experimentally. Consequently, it is likely to be metastable. Phenyl derivatives of pentazole have been synthesized. We performed the initial *ab initio* study of HN_5[5] predicting its vibrational spectra for future identification, and addressing its decomposition pathways and associated activation barriers. HN_5 was found to offer an I_{sp}=346 sec as a monopropellant, and the barrier to decomposition was found to be 19.8 kcal/mol. This study employed the new MBPT(2) analytical gradient methods previously developed under this grant.

2. The fact that HN_5 can be stabilized by replacing H by a phenyl group suggests the feasibility of using one N_5 to stabilize another, to form the bipentazole molecule [5].

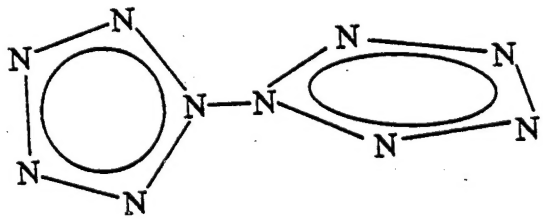

Figure 2 Bipentazole Molecule

We believe that this fascinating molecule is an outstanding candidate for synthesis. Various other pentazole derivatives have been considered, with amine (-NH_2) substituted pentazoles (H_2N-N_5) showing greater I_{sp} values than nitro O_2N-N_5 substituted ones, but electron donating substituents like NH_2 and Li also lower the activation barrier to decomposition. Electron withdrawing groups stabilize the pentazole ring.

3. Since $Be(BH_4)_2$ has one of the highest heats of formation known, we consider another experimentally unknown molecule, $LiBe(BH_4)_3$ where a third energetic BH_4 group could be added to the basic structure[2] [24].

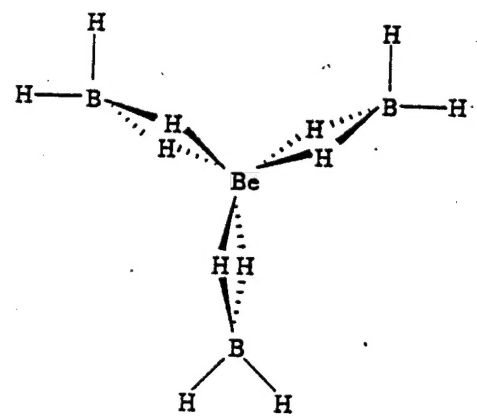

Figure 3 $Be(BH_4)_3$ Anion

We find that this molecule has a substantial barrier to losing its third BH_4 unit. Its I_{sp}=379 sec. Like bipentazole, it deserves synthesis and experimental characterization.

4. Another group of fascinating, metastable molecules are those composed of HBNCH units [3,7,18]. Our original interest in this unit arose from its isovalent equivalence to the organic analog cyclopropenyl cation.

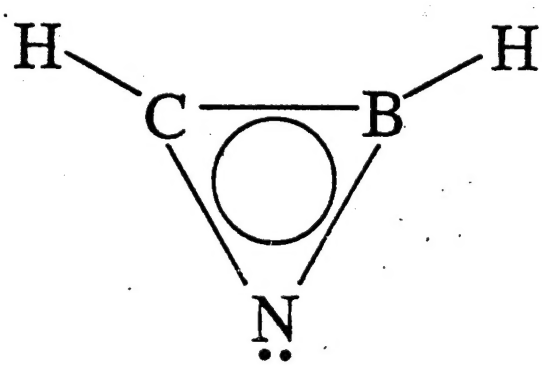

Figure 4 Cyclopropenyl Molecule

We performed an exhaustive study of the HCNBH potential energy surface [7]. When two such units are combined, a cyclic molecule of the form

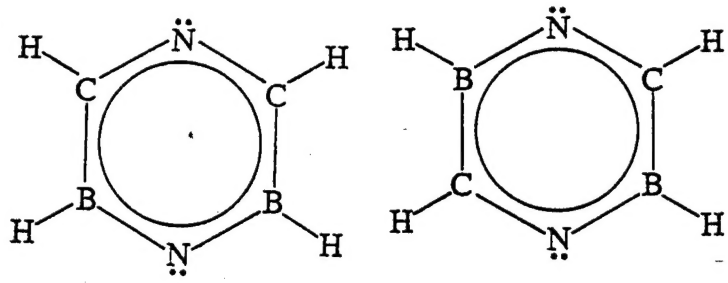

Figure 5 Cylic Dimers of HC-N-(BH)-(CH)

could be envisioned, but rather than being "benzene-like," the molecule assumes a bent form analogous to cyclohexane. We present its energetics and vibrational spectra [3, 18]. Perhaps even more intriguing is the prospect for polymers of the HCNBH unit [3, 18]!

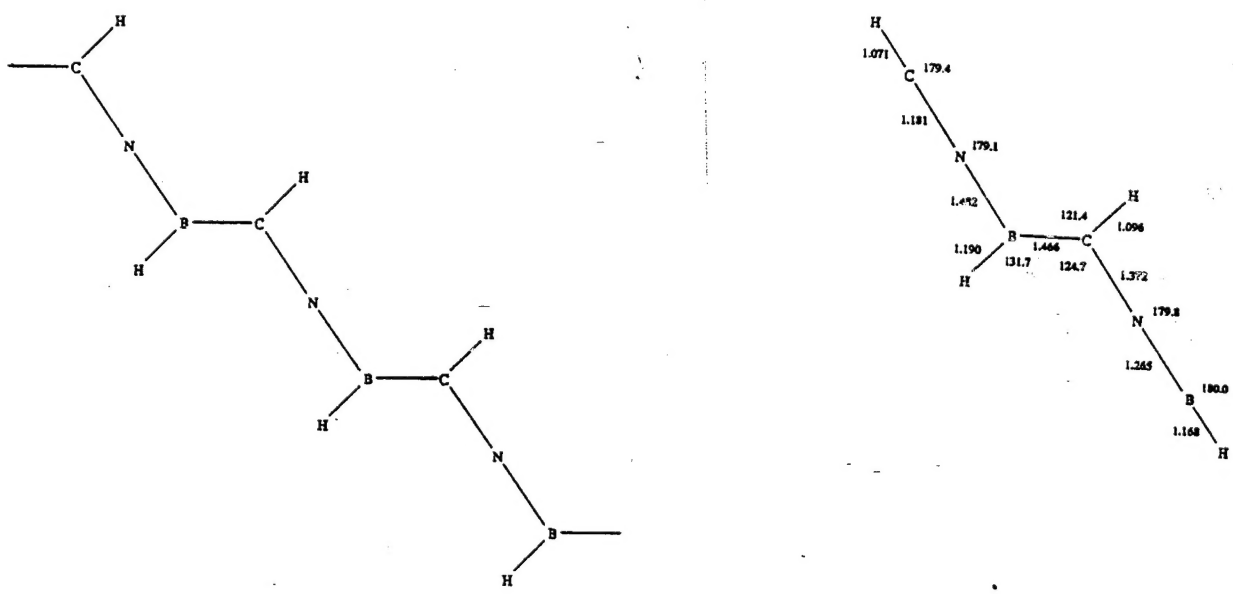

Figure 6 Polymers of N-(BH)-(CH)

None of these molecules are known experimentally, yet the cyclic and polymeric forms conform to established bonding patterns with B and C being tricoordinate, with one BN bond (1.265 Å being the triple bond typical of iminoboranes alternating with a longer single BN bond (1.482 Å), and similar alternation of CN between single (1.372 Å) and triple

bonds (1.181 Å) forms. Besides being energetic, this polymer is likely to offer an interesting semi-conductor material.

5. Other work with metastable molecules has focused on tetrahedral N_4 and the octahedral nitrogen analog of cubane, N_8[11] [6]. Both are found to be metastable; to be symmetry (Woodward-Hoffman) forbidden from decomposition into N_2 molecules; and to be very energetic. I_{sp}=489 for N_4 and 531 for N_8. The latter has been identified as the "holy grail" of metastable molecules, with concerted synthetic effort being direct toward it. We have provided MBPT(2) vibrational spectra to facilitate identification of these species.

Spectroscopic Characterization of Oxides

1. Synthesis and detonation of energetic materials involves several critical oxidation processes and associated intermediates. Carbonyl oxide,

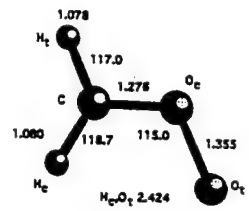

Figure 7 Carbonyl Oxide

and its cyclic isomeric form, dioxirane,

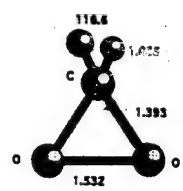

Figure 8 Dioxirane

are two key compounds in such processes. Carbonyl oxide has never been observed experimentally, though it is one of the most discussed compounds awaiting detection. We performed high level coupled-cluster CCSD(T) calculations to characterize carbonyl oxide [10]. These studies employed recently developed open-shell analytical gradients methods for CCSD(T), without which structures and vibrational frequencies would be difficult to obtain. The $\Delta H_f°(298)$ for carbonyl oxide is found to be 30.2 kcal/mol, while the barrier to isomerization to dioxirane is 19.2 kcal/mol. CCSD(T) vibrational frequencies of both species are presented to facilitate identification along with the ^{18}O isotope shifts. Shifts as high as 45cm^{-1} permit experimental discrimination between the two forms. Carbonyl oxide is found to be far more zwitterionic than lower level theoretical studies would suggest, in line with the viewpoint of synthetic chemists.

2. In the B+CO_2 reaction, the major product appeared to be an unknown OBCO species. To identify it in matrix isolation requires the application of predictive *ab initio* correlated methods to interpret the observed spectra (L. Andrews). We applied coupled-cluster theory (CCSD) and MBPT(2) to obtain the structure and vibrational spectra for OCBO [13]. Five potential structures were considered (Fig. 9).

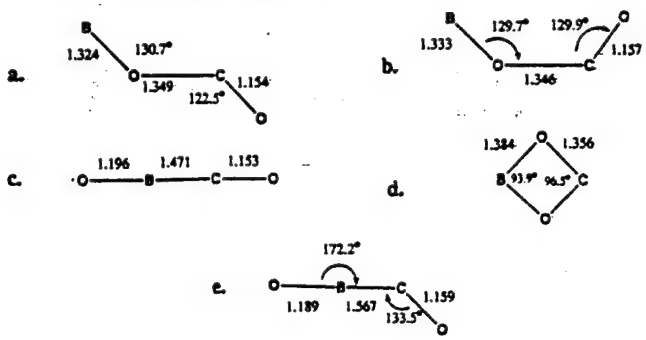

Figure 9 Calculated structural isomers of BCO_2.

All were ruled out by the computed vibrational spectra except *c* and *e*, with structure *e* being more stable by 7 kcal/mol. The CCSD results for frequencies fall within 5% of the observed and predict the isotope shifts to within an RMS error of 3.4 cm^{-1}, making assignment of the OBCO spectrum to the bent form conclusive.

3. Similar applications have been made for BO_2, where there are symmetry breaking complications for the theory, and are being made for other boron oxides to help resolve the lack of experimental energetic and spectroscopic information for the oxidation products of boron.

Methodological Advances

The ability to provide accurate energetic and spectroscopic results for candidate HEDM molecules rests upon new developments in *ab initio*, electronic structure theory. Several such advances have been accomplished in the last period of this grant. All are incorporated into the ACES II program system [4] which is now widely used throughout the world, including industry (Lubrizol, Dupont, Ford, etc.) and other government agencies (NASA Ames, DOE's Battelle, Pacific Northwest Laboratory, etc.).

1. Open shell molecules are frequently more difficult to describe accurately than those where all electrons are paired. The most widely used procedure for open shells is to start with an unrestricted Hartree Fock (UHF) reference and add electron correlation via MBPT (also known as MP) theory. However, for many problems, UHF solutions suffer from spin-contamination as the UHF function is not an eigenfunction of spin. For some problems, a restricted open shell Hartree Fock (ROHF) reference, which is a spin eigenfunction, is a better choice. However, because the ROHF method uses different Fock operators in its determination, one for doubly orbital orbitals, and one for singly occupied orbitals, it was not clear how to use an ROHF reference in MBPT calculations. We solved this problem to provide a non-iterative ROHF-MBPT method for second, third and fourth order, [2], that is

no more expensive than the usual UHF-MBPT calculations, but one that offers vastly better convergence to the exact result for spin contaminated cases. This is illustrated in Fig. 10, for the CN radical.

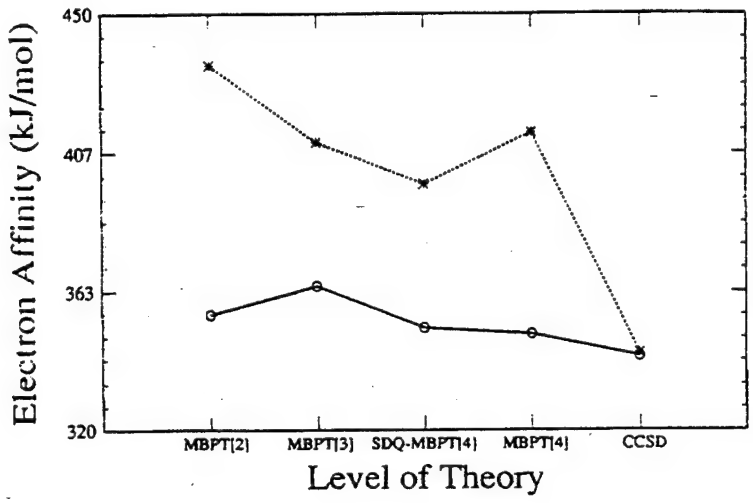

Figure 10 Electron affinity of CN radical. (O) ROHF; (*) UHF.

Note that at the ROHF-MBPT(2) level, there is good agreement with infinite order CCSD results, while UHF-MBPT(2) is far from the converged answer. Furthermore, finite order MBPT failed to rectify this failing of the UHF, spin contaminated reference.

2. To locate critical points on an energy surface, E(R), as minima or transition states, requires the facile evaluation of the forces on the atoms in a molecule, $\nabla E(R)$. Since molecules have 3N-6 degrees of freedom where N is the number of atoms, repeated calculation of E(R) in all degrees of freedom is a hopeless procedure for most polyatomic molecules. However, by also evaluating $\nabla E(R)$ *analytically*, in about the same time as E(R) itself, it is comparatively easy to locate the minimum energy geometry where the atomic forces vanish. We provided the initial ROHF-MBPT(2) analytical gradients under this grant, [2, 9] and used it in several applications to transient molecules like FCS.

3. The other primary methodological advances achieved two years ago is the general formulation and implementation of the equation-of-motion (EOM-CCSD) method for excited states, UV-visible spectra, and associated properties. This is a very ground method that shows promise of being the method of choice for excited states. The theory [11, 12, 16, 23] and several applications [14–16, 22] have been recently reported.

The basic idea of EOM-CC is that most of the dynamical correlation in a ground (or reference) state is quite similar to that in an excited, ionized, or electron attached state; but the non-dynamical correlation is quite different, and any suitable method must account for this difference.

B. Equation-of-Motion Coupled Cluster Method for Excited States

In the equation-of-motion (EOM)-CC, the reference state, which is not necessarily the ground state, is described by CC theory. The fundamental idea of EOM-CC is to describe the kth excited state wavefunction as being created from the ground state by using an excitation operator R_k, defined as a sum of single, double, etc. excitation operators:

$$R_k = \sum_m r_m(k) q_m^\dagger = r_0(k) + \sum_{i,a} r_i^a(k) \left\{ a^\dagger i \right\} + \sum_{\substack{i<j \\ a<b}} r_{ij}^{ab}(k) \left\{ a^\dagger i b^\dagger j \right\} + \ldots \tag{1}$$

i.e. a CI-like description. Amplitudes are to be determined via the EOM-CC equations. In this way, most of the correlation effects that are common to the ground and excited states are conveniently handled, allowing the excited state description to primarily focus on the essential differential correlation effects. The Schrodinger equation for the excited state $H_N = H - \langle 0|H|0\rangle)$

$$H_N|\Psi_k\rangle = \Delta E_k|\Psi_k\rangle,$$

can then be written

$$H_N R_k|\Psi_o\rangle = H_N R_k e^T|0\rangle = \Delta E_k R_k e^T|0\rangle. \tag{2}$$

Multiplying the reference state solution $H_N|\Psi_o\rangle = \Delta E_o|\Psi_o\rangle$ by R_k, and subtracting from Eqn. (2) yields the EOM,

$$[H_N, R_k]|\Psi_0\rangle = \omega_k R_k|\Psi_0\rangle \tag{3}$$

where $\omega_k = \Delta E_k - \Delta E_o$ is the excitation energy. The operators, e^T and R_k commute. Multiplying Eqn. (3) by e^{-T} gives

$$(e^{-T} H_N e^T) R_k|0\rangle = H_N R_k|0\rangle = \Delta E_k R_k|0\rangle.$$

The similarity transformed Hamiltonian, $\bar{H}_N$, is manifestly connected and exactly terminates after four T operators regardless of the number of electrons. Then with ΔE_o being the correlation correction in the reference state, $\left(\bar{H}_N\right)_{open} = \bar{H}_N - \Delta E_0$, we have

$$\left(\bar{H}_N\right)_{open} R_k|0\rangle = \omega_k R_k|0\rangle, \tag{4}$$

and there can be no contributions from the $R_k H_N$ part of the commutator in Eqn. (3), since no contractions between R_k and H_N are possible. In this way, $\bar{H}_N$ is treated as a generalized, second-quantized operator that can be written as a sum of one-body, two-body, and higher interactions:

$$H_N = \sum_{p,q} \bar{f}_{ps} \{p^\dagger q\} + \frac{1}{2!} \sum \overline{\langle pq||rs\rangle} \{p^\dagger q^\dagger sr\} + \frac{1}{3!} \sum_{\substack{p,q,r \\ s,t,u}} \overline{\langle pqr||stu\rangle} \{p^\dagger q^\dagger r^\dagger uts\} + \ldots \tag{5}$$

The $\bar{f}$ and $\langle\bar{||}\rangle$ integrals are modified or "dressed" versions of ordinary Fock matrix elements whose specific expressions in terms of intermediates composed of two-electron integrals and T amplitudes taken from the reference state CC calculation are presented elsewhere [11]. For

calculations limited to single and double excitations, i.e. EOM-CCSD, nothing contributes beyond the three-body terms.

From the definition it is clear that $\overline{H}_N$ is a non-Hermitian operator, so it has left L and R eigenvectors,

$$\langle 0|L_k(\overline{H}_N)_{open} = \omega_k \langle 0|L_k \tag{6}$$

with the same eigenvalues. $\{L_k\}$ and $\{R_k\}$ form a set of biorthogonal eigenvectors ($\langle L_k|R_k\rangle = \lambda_k \delta_{kl}$ and we are free to choose $\lambda_k = 1$). Both L_k and R_k are required to evaluate transition moments and other properties [11].

Eqns. (4) and (6) can be converted to a non-Hermitian CI-like eigenvalue problem

$$\overline{H}_N R_k = \omega_k R_k,$$
$$L_k \overline{H}_N = L_k \omega_k$$

R_k and L_k represent the coefficients for the chosen excitations. Eigenvalues and eigenvectors of H_N can be determined using a non-Hermitian modification of Davidson's method.

Since the CC amplitudes are solutions, $(\overline{H}_N)_{QP}$=0, the first column of $(\overline{H}_N)$ consists of zeros, which means the excited state solutions do not interact with the ground state, permitting the excitation energies to be directly evaluated from the sub-matrix $(\overline{H}_N)_{QQ}$. Notice $r_0(k)$ is irrelevant for the energy determination. The left eigenvector for the *referencee* state is $L_0 = 1 + \Lambda$, which exactly comes from CC analytical gradient theory, while $L_k = \Lambda_k,\ k > 0$. Consequently, EOM-CC excited states can be obtained as a byproduct of a CC analytical gradient program [11, 12, 16].

EOM-CCSD is clearly exact (i.e. the full CI) for two electrons, but as will be pointed out below, results are much better for states dominated by single excitations.

In the last couple of years under this grant we have made the initial general implementation of the EOM-CCSD method for electronic excited states and associated UV-visible spectroscopy. To illustrate the accuracy of the method we can show some comparisons to the "exact" full CI results. The latter are only possible for small systems such as the Be atom and the CH^+ molecules, but they provide useful benchmarks for methods like EOM-CCSD that can be applied to much larger systems. Results for Be are show in Tables I and 2.

Table 1. Be singlet excitation energies (in eV).[a]

	CISD[b]	MR-CCSD[c]	EOM-CCSD	full CI[d]	EXPT[d]
2s2p $^1P^0$		5.40	5.323	5.318	5.277
2s3s ^1S	7.383	6.87	6.773	6.765	6.779
$2p^2$ ^1D	7.710	—	7.139	7.089	7.05
2s3p $^1P^0$		7.50	7.465	7.462	7.462
2s3d ^1D	8.658	7.80	8.059	8.034	7.988
2s4s ^1S	8.697	8.12	8.078	8.076	8.089
2s4p $^1P^0$		8.34	8.309	8.302	8.311
2s4d ^1D	9.159	8.48	8.547	8.536	8.527
2s5s ^1S	9.221	8.62	8.583	8.600	8.595
2s5p $^1P^0$		8.72	8.700	8.693	8.694
average deviation	0.621[e]	0.07	0.016	0.000	0.018

a. [9s9p5d] basis set. Used spherical of d functions.
b. This work.
c. MRCCSD is the Fock space multi-reference method
J. Geertsen, M. Rittby and R.J. Bartlett, Chem. Phys. Lett. 164, 57 (1989); S. Pal, M. Rittby, R.J. Bartlett, D. Sinha and D. Mukherjee, J. Chem. Phys. 137, 273 (1987); M. Rittby, S. Pal and R.J. Bartlett, J. Chem. Phys. 90, 3214 (1989).
d. R. L. Graham, D. L. Yeager, J. Olsen, P. Jørgensen, R. J. Harrison, S. Zarrabian and R. J. Bartlett, J. Chem. Phys., 85, 6544 (1986).
e. The large error is due to the lack of adequate core correlation in the excited states. If the core 1s is frozen, this error nearly vanishes, as only a two-electron system is being described. Note that EOM-CCSD does not have this problem.

Table 2. Be triplet excitation energies (in eV)

	MR-CCSD	"closed-shell" EOM-CCSD[a]	open-shell EOM-CCSD[b]	full CI	EXPT
2s2p $^3P^0$	2.80	2.729	2.723[d]	2.733	2.725
2s3s ^3S	6.49	6.447	6.433[d]	6.444	6.457
2s3p $^3P^0$	7.35	7.301	7.290	7.295	7.303
$2p^2$ $^3P^e$	—	7.510	7.414	7.423	7.401
2s3d ^3D	7.78	7.748	7.730	7.741	7.694
2s4s ^3S	8.01	7.991	7.973	7.985	7.998
2s4p $^3P^0$	8.34	8.278	8.267	8.272	8.283
2s4d ^3D	8.47	8.456	8.437	8.449	8.423
2s5s ^3S	8.58	8.566	8.548	8.560	8.556
2s5p $^3P^0$	8.70	8.691	8.681	8.686	8.688
2s6s ^3S	8.92	8.893	8.874	8.886	8.823
average deviation	0.038	0.013	0.009	0.000	0.023

a. This work. Used $2s^2$ ^1S ground state reference.

b. This work. For ^3S and ^3D states, used 2s3s ^3S reference. For ^3P states, used 2s2p $^3P^0$ reference.

The comparison between the EOM-CC and full CI numbers seen in Tables I and 2 is remarkable, though Be with only two valence electrons is not the most challenging example. With the exception of the double excitation $2s^2 \rightarrow 2p^2$, the EOM-CCSD energies are all within 0.03eV from the full CI values. Most excitations are within 0.01eV. Even the double excitation value is within 0.1eV. We will discuss improvements for states dominated by double excitations below.

Despite ground state Be being a closed-shell atom, to demonstrate application to open shells we can still calculate "excitation" energies using an excited state as the reference. Excitation energies using the $2s2p$ $^3P^0$ and $2s3s$ ^3S excited states as the couple-cluster reference states relative to a UHF single reference (an ROHF reference causes only a slight difference). These appear in Table 2 in the column labeled "open-shell EOM-CC." These numbers compare very well with the ordinary "closed-shell EOM-CC" results. On average the "open-shell" numbers show a slightly smaller average error (0.009) that is primarily caused by the superior description of the $2p^2$ $^3P^e$ double excitation state, as it is a single excitation relative to the 2s2p $^3P^0$ reference. Clearly, the energies calculated from different reference states are consistent, providing great flexibility in their choice.

In terms of the left $\langle\tilde{\Psi}|$ and right $|\Psi\rangle$ eigenvectors, the definition of the dipole strength is

$$D_{K_g} = \langle\tilde{\Psi}_g|\vec{r}|\tilde{\Psi}_K\rangle\langle\Psi_K|\vec{r}|\Psi_g\rangle \tag{7}$$

from which the oscillator strength is

$$f_L = \frac{2}{3}\omega_{K_g} D_{K_g}$$

Note the transition moment is not well defined, although the actual observable, the dipole strength, is. In this way, Eqn. (7) provides a CI-like approximation to this quantity.

As a first test of the accuracy of oscillator strengths obtained within the framework presented here, calculations have been carried out on the two systems where full configuration interaction (FCI) results are available. Table 3 documents excitation energies and dipole strengths for all optically allowed transitions that were addressed in the FCI calculations. Also included are approximate excitation levels (AEL) that act as a measure of the number of electrons that are excited from the CCSD ground state to form the excited states. The AEL is defined by the equation

$$AEL = \frac{1}{2}\sum_p |\rho_{pp}^K - \rho_{pp}^g| \tag{8}$$

where both the ground and excited reduced density matrices are expressed in the quasiparticle (approximate natural orbital) basis that diagonalizes the ground state CC density [11]. It should be clear to the reader that any AEL significantly larger than unity should be regarded with suspicion.

For beryllium, excitation energies and dipole transition strengths obtained in the present calculations are in nearly perfect agreement with the FCI results. Nevertheless, since the EOM-CCSD method is exact for two electrons, and Be ($1s^2$ $2s^2$) has a separated pair structure, the beryllium atom is an "easy " problem. The processes studied here are essentially single-electron

transitions (all AEL) values are near 1.05) and the correlation effects in this system are dominated by the two valence electrons.

A more difficult test is provided by the CH^+ molecule, which contains more electrons and exhibits strong nondynamical electron effects in its ground electronic state via interaction of the $1\sigma^2 2\sigma^2 3\sigma^2$ and $1\sigma^2 2\sigma^2 1\pi^2$ electronic configurations. Due to this important configuration mixing, one expects some of the low-lying electronic states to have appreciable double-excitation character, as confirmed by the AEL values listed in the rightmost column of Table 3. It can be seen that the closest coincidence of FCI and EOM-CCSD results for excitation energies and oscillator strengths occurs for the transitions near 3.2 and 13.5 eV, which both have associated AEL values below 1.1. Differences between FCI and EOM-CCSD dipole strengths for transitions to the third $^1\sum^+$ and second $^1\prod$ state are larger [error of 5.26% (AEL=1.13) and 17.69% (AEL=1.240, respectively]. The quantitative agreement between FCI and EOM-CCSD for the dipole strength of the nearly pure double excitation at 8.549 eV is fortuitous.

While the limited body of FCI excitation energies and oscillator strengths in the literature prevents us from drawing many conclusions from the present set of calculations, it appears that the EOM-CCSD method gives reliable values for dipole strengths and excitations energies (and, therefore, oscillator strengths) for electronic transitions dominated by single excitations. More recently, we have considered effects of triple excitations [20], which alleviate most of the failing for doubly excited states. We are currently using EOM-CCSD to obtain potential energy surfaces for Li embedded in a cryogenic H_2 lattice to help model such embedded solids.

Table 3. EOM-CCSD and full configuration interaction excitation energies and dipole strengths for the lowest optically allowed transitions in CH^+ and the beryllium atom. Also listed are the approximate excitation levels (AEL) for each process.

	Final state	Excitation energy (eV)		Dipole strength (a.u.)		AEL[a]
		EOM-CCSD	FCI	EOM-CCSD	FCI	
Be[b]	$^1P(2s2p)$	5.318	5.314	3.564	3.549	1.07
	$^1P(2s3p)$	7.465	7.460	0.021	0.022	1.06
	$^1P(2s4p)$	8.306	8.300	0.000 102	0.000 121	1.05
CH^{+c}	$^1\Sigma^+$	9.109	8.549	0.025	0.025	1.96
	$^1\Sigma^+$	13.580	13.525	1.073	1.080	1.03
	$^1\Sigma^+$	17.315	17.217	0.720	0.684	1.13
	$^1\Pi$	3.261	3.230	0.095	0.090	1.03
	$^1\Pi$	14.454	14.127	0.692	0.588	1.24

a. Approximate excitation level.
b. FCI results from H. Koch and R.J. Harrison, J. Chem. Phys. **95**, 7479 (1991).
c. FCI results from J. Olsen, A.M. Sanchez de Meas, H.J. Aa Jensen and P. Jørgensen, Chem. Phys. Lett. **54**, 380 (1989).

References:

1. D.H. Magers, E.A. Salter, R.J. Bartlett, C. Salter, B.A. Hess, Jr., and L.J. Schaad, "Do Stable Isomers of N_3H_3 Exist?" J. Am. Chem. Soc. **110**, 3435 (1988).

2. W.J. Lauderdale, J.F. Stanton. J. Gauss, J.D. Watts and R.J. Bartlett, "Many-Body Perturbation Theory with a Restricted Open-Shell Hartree-Fock Reference," Chem. Phys. Lett. **187**, 21 (1991).

3. I. Cernusak, M. Urban, P. Ertl and R.J. Bartlett, "$C_2H_4B_2N_2$: A Prediction of Ring and Chain Compounds," J. Am. Chem. Soc. **114**, 10955 (1992). (Rapid Communication).

4. J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale and R.J. Bartlett, "The Aces II Program System," Int. J. Quantum Chem. **S26**, 879 (1992).

5. K. Ferris and R.J. Bartlett, "Hydrogen Pentazole: Does It Exist?" J. Am. Chem. Soc. **114**, 8302 (1992). (Rapid Communication).

6. W.J. Lauderdale, J.F. Stanton and R.J. Bartlett, "Stability and Energetics of Metastable Molecules: Tetraazatetrahedrane (N_4), Hexaazabenzene (N_6) and Octaazacubane (N_8), J. Phys. Chem. **96**, 1173 (1992).

7. I. Cernusak, S. Beck and R.J. Bartlett, "Potential Energy Surface of Borazirene (HCNBH)," J. Phys. Chem. **96**, 10284 (1992)

8. J.F. Stanton, J. Gauss, R.J. Bartlett, T. Helgaker, P. Jørgensen and H.J. Aa. Jensen, "Interconversion of Diborane(4) Isomers," J. Chem. Phys. **97**, 1211 (1992).

9. W.J. Lauderdale, J.F. Stanton, J. Gauss, J.D. Watts and R.J. Bartlett, "Restricted Open-Shell Hartree-Fock Based Many-Body Perturbation Theory: Theory and Initial Application of Energy and Gradient Calculations," J. Chem. Phys. **97**, 6606 (1992).

10. D. Cremer, J. Gauss, E. Kraka, J.F. Stanton and R.J. Bartlett, "A CCSD(T) Investigation of Carbonyl Oxide and Dioxirane. Equilibrium Geometries, Dipole Moments, Infrared Spectra, Heats of Formation and Isomerization Energies," Chem. Phys. Lett. **209**, 547 (1993).

11. J.F. Stanton and R.J. Bartlett, "The Equation of Motion Coupled-Cluster method. A Systematic Biorthogonal Approach to Molecular Excitation Energies, Transition Probabilities and Excited State Properties," J. Chem. Phys. **98**, 7029 (1993).

12. D.C. Comeau and R.J. Bartlett, "The Equation-of-Motion Coupled-Cluster Method: Applications of Open- and Closed-Shell Reference States," Chem. Phys. Lett. **207**, 414 (1993).

13. T.R. Burkholder, L. Andrews and R.J. Bartlett, " Reaction of Boron Atoms With Carbon Dioxide. Matrix and *Ab Initio* Calculated Infrared Spectra of OBCO," J. Phys. Chem. **97**, 3500 (1993).

14. J.F. Stanton and R.J. Bartlett, "Does Chlorine Peroxide Exhibit a Strong Ultraviolet Absorption near 250nm?" J. Chem. Phys. **98**, 3022 (1993).

15. N. Oliphant and R.J. Bartlett, "The Theoretical Determination of Charge Transfer and Ligand Field Transition Energies for $FeCl_4^-$ Using the EOM-CC Method," J. Am. Chem. Soc. **116**, 4091 (1994). (Rapid Communication)

16. R.J. Bartlett and J.F. Stanton, "Application of Post Hartree-Fock Methods: A Tutorial," in *Revs. Comp. Chem.* **5**, pp. 65–169, 1994, VCH Publishers, Eds. K.B. Lipkowitz and D.B. Boyd.

17. H. Sekino and R.J. Bartlett, "Nuclear Coupling Constant Calculation by the Equation of Motion Coupled-Cluster Theory," Chem. Phys. Lett., **225**, 486 (1994).

18. I. Cernusak, P. Ertl, M. Urban and R.J. Bartlett, "$C_2H_4B_2N_2$: *Ab Initio* Prediction of Structure and Properties of Ring and Chain Compounds," J. Phys. Chem. **98**, 8653 (1994).

19. J.D. Watts and R.J. Bartlett, "On the Existence of BH_5," J. Amer. Chem. Soc. **117**, 825 (1995) (Rapid Communication)

20. J.D. Watts and R.J. Bartlett, "Economical Triple Excitation Equation-of-Motion Coupled-Cluster Methods for Excitation Energies," Chem. Phys. Lett., **233**, 81 (1995).

21. M. Nooijen and R.J. Bartlett, "Equation of Motion Coupled Cluster Method for Electron Attachment," J. Chem. Phys., **102**, 3629 (1995).

22. S.R. Gwaltney and R.J. Bartlett, "An Application of the Equation-of-Motion Coupled Cluster Method to the Excited States of Formaldehyde, Acetaldehyde, and Acetone," Chem. Phys. Lett. **241**, 26 (1995).

23. R.J. Bartlett, "Coupled Cluster Theory: An Overview of Recent Developments," in *Modern Electronic Structure Theory*, p. 1047 ed. D.R. Yarkony, World Scientific Publishing Co. Ltd., Singapore, (1995).

24. W.J. Lauderdale, J.F. Stanton and R.J. Bartlett, "The Novel Anion Be $(BH_4)_3^-$," to be published.

25. S.A. Perera, P. von Schleyer and R.J. Bartlett, "Predicted NMR Coupling Constants and Spectra for Ethyl Carbocation: A Fingerprint for Nonclassical Hydrogen-Bridged Structures," J. Am. Chem. Soc., **117**, 8476 (1995) (Rapid Communication).

26. J.D Watts and M.J. Huang, "Theoretical Characterization of the Ground States of HNS and NSH", J. Phys. Chem. **99**, 5331 (1995).

Invited Presentations Assisted by HEDM Grant (1992–1995)

November 1995 — "Electronic Excited States of Organic Molecules", Joint Regional ACS Meeting, Memphis, TN.

October 1995 — "Carbon Cluster C_2—C_{10}: The Synergism Between Theory and Experiment", Korean Advanced Institute of Science and Technology, Taejon, Korea.

October 1995 — "An Introduction to Coupled-Cluster Methods and Other Correlated Approaches", Postec University, Pohang, Korea.

October 1995– "Coupled-Cluster Theory as a Unified Approach to Molecular Spectroscopy: Vibrational, Electronic, and NMR," Korean Chemical Society, Pusan, Korea

September 1995 — "Equation-of-Motion Coupled-Cluster Method for Excited, ionized and Electron-Attached States", Molecular Quantum Mechanics: Methods and Applications Conference, in Memory of S.F. Boys and in Honor of I. Shavitt, University of Cambridge, Cambridge, England.

August 1995 — "Excited States Using the Equation–of–Motion Coupled–Cluster Method," 12th Canadian Symposium on Theoretical Chemistry, University of New Brunswick, Fredericton, Canada

June 1995 — "Analogues of Tetrahedral N_4 as Potential High-Energy Molecules," Air Force High Energy Density Materials Contractors' Conference, Woods Hole, MA

January 1995 — Air Force Office of Scientific Research HEDM Theory-Synthesis Workshop, Palmdale, CA

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